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MOLDING STAMP FOR APPLICATION OF MICROSTRUCTURES ON ARTICLES, METHOD THERETO AND ALSO EDIBLE ARTICLES PRODUCED THEREFROM

[Abformstempel zum Aufbringen con Mikrostrukturen auf Gegenstände, Verfahren hierfür sowie danach hergestellter eßbarer Gegenstand]

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The invention relates to a molding stamp for application of microstructures, in particular of surface holograms, diffractive structures or holographic optical elements, onto an article, and to a suitable method thereto.

Microstructures of the stated kind, in particular surface holograms, are widely used today. They appear, for example, on numerous check cards or even on software products as evidence of authentication. Such microstructures have a lattice spacing of about 1 μm and a structure depth of about 0.1-0.2 μm, which corresponds to a density of the printed points of 5000 to 10,000 points/cm.

With regard to the holograms, a distinction is made between two types: volume holograms and surface holograms. Now in the volume holograms, the microstructure forming the hologram is located within an optically transparent layer with a thickness which is much greater than the wavelength of the incident light. Thus the microstructure forms a three-dimensional lattice at which the light is diffracted. The surface of such volume holograms is normally smooth. But surface holograms, and only these are of interest here as a part of the present invention, are formed by a single microstructure plane having the configuration of microscopic depressions on the surface of a body. The body itself need not necessarily be transparent in this case. The diffraction efficiency of surface holograms is less than that of volume holograms, but surface holograms can be easily duplicated by means of a molding stamp.

For satisfactory application of a microstructure, which can be, for example, a surface hologram, onto an article, the used molding stamp must meet a number of requirements. Today, usually nickel shims are used as molding stamps, which were produced from an original or master hologram. These nickel shims have a very stiff surface and can thus apply the microstructure under pressure, ideally on a 1:1 basis onto the article. Furthermore, they have a high imaging quality and are thus readily capable first to pick up the microstructure to be transferred, and they have a long service life so that numerous copies can be produced with no loss in quality.

The materials onto which the microstructures are to be transferred by means of said molding stamp are plastic foils, for example, polyester foils, but also surface laminated paper which exhibits a plastic behavior under heat, so that by means of the molding stamp, the microstructure present on the latter can be imprinted under pressure and/or temperature into the plastic or into the laminated paper. Also, radiation-hardening lacquers are suitable for picking up microstructures. The molding stamp herein is pressed into the unpolymerized or graft-polymerized lacquer layer and the lacquer is then hardened in contact with the molding stamp. After hardening, the molding stamp is removed. Specifically in the widely used molding on foils and paper, the molding stamp must have an extremely strict planarity since otherwise the difference in contact pressure over the surface of the molding stamp will become too great, so that an irregular and thus deteriorated molding will result.

From the requirements described above for known molding methods, limitations are encountered with regard to the materials and also with regard to the articles onto which the microstructures are to be applied.

The invention is based on the problem of specifying a solution which overcomes the limits of conventional molding methods and which allows the molding of microstructures onto articles and materials which formerly could not be equipped with microstructures. Now the term "microstructures" is understood here to mean in particular surface holograms, diffractive structures or holographic optical elements.

To solve this problem, the invention discloses a molding stamp which consists of a hardening and after the hardening flexible plastic, whose volume shrinkage during hardening amounts to at most about 5% and which has a surface tension of less than about 0.03 N/m. Thus it is possible to produce microstructures not only on planar articles, but rather inherently also on articles with a curved, three-dimensional surface. Furthermore, due to the use of a flexible plastic molding stamp,

microstructures can be applied onto materials, for example, onto chocolate, onto which microstructures could not be applied by using conventional molding stamps.

Basically, a plastic to be used for manufacture of the molding stamp according to the invention can be any material which is castable and which can make moldings at the molecular level, that is, which has the ability to pick up and/or to impart an extremely tiny microstructure, which can be hardened into a flexible but shape-resistant body, which has only a small volume shrinkage after hardening and which has a low surface tension. One such flexible molding stamp can also be pulled off fragile materials due to its elasticity and flexibility after the molding process, so that both sensitive materials and also uneven surfaces and three-dimensional articles can be provided with a microstructure. Due to the low surface tension, no residues will remain in the molding stamp which can adversely affect the quality of the next microstructure produced by the molding stamp. The low volume shrinkage is a prerequisite for a good transfer of the master surface hologram onto the molding stamp. Preferably the volume shrinkage of the plastic used for production of the molding stamp is thus only about 1% or less, and the surface tension of the plastic should be less than 0.02 N/m.

The production of a molding stamp used in the invented method will be explained briefly below; in the selected embodiment this molding stamp is to allow the duplication of a surface hologram. The mode of production initially does not differ from the production of conventional nickel molding stamps. For example, first in a conventional manner the desired hologram is exposed in a photographic, silver halide emulsion, which is applied onto a glass plate or onto a plastic carrier. The holographic information is then located in the interior of the photo emulsion as a phase- or absorption-lattice and is thus not suitable for molding. Therefore, in a second step, by optical means, a copy of the formed hologram is created in a photoconductive, thermoplastic layer. To do so, the photoconductive, thermoplastic layer is first placed onto a conductive carrier, e.g., a metal plate, and then a static charge is

applied onto the surface of the photoconductor by a suitable method. In a subsequent exposure, the charged surface of the photoconductor is irradiated with the diffraction pattern emanating from the initially produced hologram and with an additional reference radiation of the same wavelength. The interference of the two wave fields on the surface of the photoconductor results in regions with high and with low light intensity. At the sites of high light intensity, the electrical conductance of the photoconductor increases significantly, so that at these sites due to photoconductance, a charge recombination occurs with the metal carrier resident at a reference voltage or at ground potential. At the sites of low light intensity, the original charge distribution remains generally unchanged. After completion of the exposure, on the surface of the photoconductor a latent charge carrier pattern remains which contains the holographic information. Due to the locally different charge concentrations, locally different electric field intensities also prevail. The thermoplastic photoconductor is now heated to a temperature above the softening point thereof. The locally different electrical field intensities consequently have corresponding electrostatic forces which cause the now plastic surface to be plastically deformed according to the local force acting thereon, and the surface relief is formed. After cooling of the thermoplastic photoconductor, this surface relief, which already represents the desired surface hologram, is fixed. The surface hologram produced in this manner is also called the master surface hologram (or original hologram).

Now in a conventional manner, through galvanic washing of nickel onto this master surface hologram, a nickel molding stamp is produced. But in contrast to this, for producing of a plastic molding stamp according to the invention, first the plastic is produced. The used plastic normally relates to a mixture of at least two components, namely binders and hardeners, which are mixed immediately before use. Alternatively, a photo-polymerizable plastic can be used, which hardens, e.g., under UV light. These pourable, viscous materials can be degassed in a vacuum in order to produce a homogeneous

molding material. Next, the still polymerized material is cast onto the master surface hologram and hardened, depending on the selected binder/hardener combination, within a few minutes or even over several hours, to obtain a shape-stable, flexible plastic molding stamp which can then be pulled off the master surface hologram.

Particularly suitable plastics for production of the molding stamp used in the invented method are a series of silicones, such as those used in the dental field. These silicones consist of two components which crosslink at room temperature. A distinction is made between condensation and addition crosslinking types. For purposes of the present invention, both types are quite suitable. Silicones of this kind are subject to very little volume shrinkage of about 1% during the crosslinking or hardening process. In addition, these silicones have a low surface tension and polarity, they are resistant to cleaning agents like soap solutions and alcohols, are mechanically resistant and temperature resistant. The hardness (Shore hardness) of these silicones in the hardened state can be between A 12 (extremely soft) and A 75 (very hard) and are thus well adapted to the particular application. Some other, highly suitable plastic materials are the polyurethanes.

Plastic molding stamps of this kind in connection with the invented method allow the application of microstructures onto materials and/or articles which did not allow the application of microstructures in a suitable manner using conventional molding stamps. For example, it is possible with the invented method to apply microstructures onto edible articles or materials. As examples, we can mention gelatins (in the form of a foil, as a coating or as a shaped body), fats (plant and animal origin, in hardened, partly hardened or unhardened form), slightly or non-hygroscopic sugars, starches (in the form of an emulsion, as a coating or as a shaped body), fruit gum and fruit gum mixtures, gum Arabic (as a coating) and combinations of the mentioned materials. Only the grain size of the particular material is a limiting factor; that is, the material onto which a microstructure is to be applied must have a grain size in the

molecular range in order to pick up the microstructure. Even the presence of a coarse grain can allow production of a microstructure onto the material, if—as is frequently the case for foods—at least the binder (fat, starch, sugar, emulsions, etc.) has a sufficiently fine grain size and the coarser grain is completely enclosed so that the microstructure to be formed is picked up primarily by the binder. In order to ensure a high resistance of the molded microstructures, care must also be taken that the material onto which the microstructure is applied, has no or low hygroscopic properties, since otherwise due to water absorption, a swelling of the surface layer will occur, so that the microstructure is destroyed. Of course, materials onto which the microstructures have been applied, also may not be heated too much, since any softening and/or melting of the material will likewise destroy the microstructure.

To protect against moisture and for an increased resistance to mechanical factors, according to one preferred embodiment of the invented method, the applied microstructure is coated with a protective layer. Suitable protective layers in this regard are, for example, gum Arabic or even a thin layer of fat. In the case of non-edible articles, as protective layer one can use, for example, a clear lacquer which can also be flexible or scratch-resistant, depending on the application.

The invented method is particularly suitable, for example, for application of microstructures onto chocolate. As tests in the field of the invention have shown, microstructures cannot be transferred to chocolate with conventional molding stamps, since either the chocolate material fractures right during the printing of the molding stamp, or it breaks when the chocolate material is poured onto the molding stamp and then the molding stamp is removed. Moreover, chocolate residues adhering to the molding stamp make the molding stamp useless for the next imprinting step. The flexibility and low surface tension of the invented plastic molding stamp provides a remedy here and allows the application of microstructures even onto three-dimensional articles of chocolate, such as Easter rabbits, Easter eggs, pralines and such.

To increase the luminance of the applied microstructure, according to one embodiment of the invented method, the microstructure is vapor coated with a thin layer of gold. The vapor coating with gold (layer thickness about 10-20 nm) is suitable both for transparent materials (e.g., gelatins) and also for light-impermeable materials (e.g., chocolate), since the thin layer of gold follows the imprinted microstructure in a nearly ideal manner and does not blanket it. Moreover, gold has been approved for use in the food industry so that even microstructures on edible materials can be vapor coated with a layer of gold. Alternatively, the applied microstructure can be covered with a fine-grain (< 20 nm) gold or silver paint approved for food use. The paint and the reflective particles contained therein likewise form the microstructure. The relatively thick layer of paint, however, causes the microstructure to be blanketed and thus is no longer visible from the application side. Painting with gold or silver paint is thus suitable only for transparent microstructure carrier materials in which the microstructure with enhanced luminance can be viewed from behind through the transparent carrier. It is preferable that the sensitive microstructure in this alternative be protected between the transparent carrier and the gold or silver paint.

Due to the flexible plastic molding stamp it is now possible with the invented method to apply microstructures directly onto an article during the manufacturing process thereof.

For example, the flexible plastic molding stamp can form a part of a bubble, cast or injection mold, so that, for example, a plastic body (bottle, can, etc.) can be equipped with the microstructure on the surface thereof right during the manufacture. It is possible to apply a company logo or another recognition symbol of a company in this manner to any plastic product of this company. In particular in the case of smaller articles, the plastic molding stamp can also represent the entire cast mold or the lining thereof.

Basically, with the invented method all materials can be embossed which are molecularly moldable, which can be plastically deformed by heat and/or pressure, which can harden in contact with the molding stamp and which exhibit a low shrinkage. A release of the molding stamp is easily possible due to the low surface tension of the used plastics and due to the flexibility of the molding stamp.

A number of application examples of the invented method are presented below.

Example 1

A child's lollipop made of colored, but transparent material, is to be equipped with a surface hologram which is to remain visible for as long as possible. Thus, the lollipop body is produced from two halves, and one half is equipped with a surface hologram by means of the invented method. The other half of the lollipop body is then bonded to the first half so that it acts as protector for the surface hologram; i.e., the surface hologram is located inside the lollipop body. Based on the transparency of the lollipop material it is still possible to see the hologram from the outside, and for as long as the core of the lollipop has not been destroyed by the licking process. In an alternative design embodiment, both mutually facing surfaces of the lollipop halves can be equipped with surface holograms. When viewing the lollipop from different viewing angles, different holograms can be seen. Preferably the surface holograms on the mutually facing surfaces of the lollipop halves are recessed somewhat into the corresponding surface, so that damage to the hologram when joining the two halves of the lollipop will be avoided.

Example 2

A chocolate body is equipped with a surface hologram by means of the invented method. To protect the surface hologram, a layer of transparent sugar material is applied onto the chocolate body. If desired, the surface hologram can first be vapor coated with gold in order to increase its brilliance.

Example 3

Chocolate candies are to be equipped with a surface hologram. To do so, the cast mold of the chocolate candies or a portion thereof is formed by a flexible plastic molding stamp according to the invention. The liquid chocolate material is filled into this mold, and care must be taken that the temperature difference between the casting temperature and the solidification temperature is not too large. Otherwise, due to the different expansion behavior of molding stamp and chocolate, the molded hologram will break in the cooling phase. A temperature difference of about 10°C to 20°C is usually not critical. When filling the chocolate material, chocolate material and molding stamp should have roughly the same temperature in order to avoid solidification shock which can adversely impact the precise formation of the surface hologram.

Example 4

Gelatin is provided with surface holograms in a rotation engraving method (see Figure 1). A gelatin foil sheet 10 is passed through the roller gap between two rollers 12, 14 rotating in opposite directions. The upper roller 12 bears the molding stamp, which here has the structure of a flexible embossing cylinder 16. Directly before passing through the roller gap, the gelatin foil sheet 10 is moistened slightly on the top side onto which the surface hologram is to be applied. This slight addition of moisture—water

vapor condensing onto the surface of the foil sheet is sufficient—causes the top gelatin layer to soften somewhat, which promotes the imprinting of the surface hologram.

The example described above in connection with the production of the gelatin foil can be transferred with little change to the production of plastic foils.

Alternatively, a gelatin foil sheet can be equipped with surface holograms right during the manufacture thereof (see Figure 2). Liquid gelatin material is applied through a gap-rake system of constant thickness onto a roller 12' whose design corresponds to the roller 12 illustrated in Figure 1. The applied gelatin material hardens on the flexible embossing cylinder 16' and is then pulled off the roller 12' by means of a pulling roller 18 and then additionally processed.

Example 5

By means of an injection mold 20 (see Figure 3) a plastic container is to be produced which is equipped on the outside thereof with a surface hologram. Thus, the flexible plastic molding stamp 25 is placed into the outer mold 22 of the injection mold 20 at the desired location so that the molded surface hologram comes into contact with the plastic 26 injected between inner mold 24 and outer mold 22 and so that the surface hologram appears on the outer surface of the bottle. Due to the flexible nature of the molding stamp 25, said stamp can also be located in a curved region of the outer mold 22.

Example 6

The visible surface of cathode ray tubes 30 (see Figure 4) is to be made non-reflective. To do so, a transparent, hardening lacquer 34 is applied to the surface 32 of the glass. This lacquer can be a two-component lacquer or a radiation hardening lacquer. The application onto the partly bulged screen surface 32 can occur by spinning, raking, painting or such. Onto the still unhardened lacquer 34, a

flexible molding stamp 36 adapted to the shape of the picture tube 30 is pressed down in a form-fitting manner and imprints a microstructure in the lacquer 34 which produces a destructive interference. Now the lacquer hardens in contact with the molding stamp 36 either by itself (in the case of a two component lacquer) or by addition of a suitable radiation (for example, UV radiation 37 in the case of a UV hardening lacquer). In the latter case, the molding stamp 36 must be sufficiently transparent for the employed radiation. As material for the molding stamp 36, we can use, for example, transparent silicone. Preferably the material of the molding stamp 36 is also UV stable in order not to affect the flexibility after exposure to the UV radiation. After complete hardening of the lacquer 34, the molding stamp 36 is pulled off and is available for the next molding process.

Alternatively, in the example just described, first the lacquer 34 can be applied onto the molding stamp 36 and then the molding stamp 36 with the lacquer 34 can be pressed onto the surface 32 of the picture screen.

Finally, the concept of "destructive interference" will be explained in greater detail. In "normal" surface holograms, the lateral spacing between two neighboring wave peaks is on the order of about 1 μm, whereas the amplitude, that is, the maximum extent perpendicular to the surface, is about 0.1-0.3 μm. In zero-order diffraction patterns, however, the lateral spacing can be so small that a constructive interference produced by diffraction no longer can occur. Such structures are known by the name "moth eyes." This can be explained based on the lattice equation:

$$n \cdot \lambda = g \cdot \sin(\varphi)$$

in which n represents the ordinal number of the diffraction, λ is the used wavelength (visible range: λ = 400 nm to 750 nm), g is the lateral spacing, and φ is the angle under which the n-th degree

constructive interference occurs. With $n = 1$ (first diffraction) and the color green ($\lambda = 555$ nm), with a spacing $g < 555$ nm we have no constructive interference, since the angle φ no longer exists. However, destructive interference occurs, since here the even numbered multiples of the wavelength (1 λ, 2 λ, 3 λ…) do not overlap, but rather 0.5 λ, 1.5 λ, 2.5 λ, … By means of such structures, the reflectivity of glass plates, for example, can be reduced from 4% to less than 0.5%, without affecting the transparence of the glass.

Claims

1. Molding stamp for application of microstructures, in particular of surface holograms, diffractive structures or holographic optical elements, onto an article, characterized in that the molding stamp consists of a hardening and after the hardening flexible plastic, whose volume shrinkage during hardening amounts to at most about 5% and which has a surface tension of less than about 0.03 N/m.

2. Molding stamp according to Claim 1, characterized in that the volume shrinkage of the plastic amounts to about 1% or less.

3. Molding stamp according to Claim 1 or 2, characterized in that the plastic has a surface tension of less than 0.02 N/m.

4. Molding stamp according to one of Claims 1-3, characterized in that it is light-permeable and has preferably a transmission window for light in the range of UV to IR.

5. Molding stamp according to Claim 4, characterized in that the plastic is UV stable.

6. Molding stamp according to Claim 1-6, characterized in that the plastic is a condensation crosslinked or addition crosslinked silicone.

7. Molding stamp according to one of Claims 1-6, characterized in that the plastic is a radiation-hardened plastic.

8. Molding stamp according to one of Claims 1-7, characterized in that the plastic is a polyurethane.

9. Method for application of microstructures, in particular of surface holograms, diffractive structures or holographic optical elements, onto an in particular nonplanar surface of an article, with the following steps:

- Preparation of a molding stamp according to one of the preceding claims whose stamp surface is equipped with the microstructure to be applied,
- bringing this molding stamp into contact with the surface of the article in such a manner that the microstructure is molded onto the surface of the article, and
- separation of the molding stamp from the surface of the article.

10. Method according to Claim 9, characterized in that the molding stamp is a blow mold, cast mold or injection mold or a portion of one such mold for production of the article onto which the microstructure is applied.

11. Method according to Claim 9 or 10, characterized in that the article onto which the microstructure is applied, consists of a plastic which is hard or rubbery-flexible after hardening.

12. Method according to Claim 9 or 10, characterized in that the article onto which the microstructure is applied, is edible.

13. Method according to Claim 12, characterized in that the surface of the article is made of gelatin, fat, sugar, starch, fruit gum, gum Arabic or a combination of the above-stated substances.

14. Method according to Claim 12, characterized in that the article consists at least in part of chocolate.

15. Method according to one of Claims 12-14, characterized in that after application of the microstructure onto the article, the microstructure is coated with an edible protective layer, in particular of gum Arabic or fat.

16. Method according to one of Claims 9-14, characterized in that after application of the microstructure onto the article, the microstructure is coated with a thin layer of gold.

17. Method according to one of Claims 9-16, characterized in that the applied microstructure produces a zero-order interference (destructive interference).

18. Edible article, characterized by a microstructure which has been applied by a method according to one of Claims 9-17.

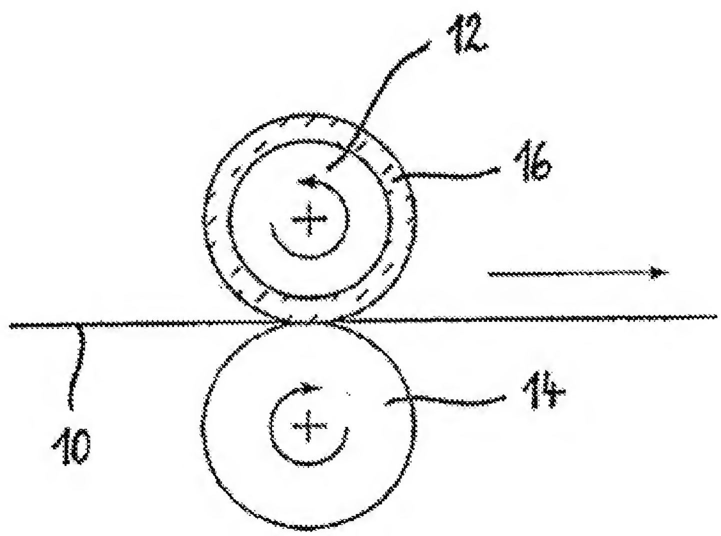

Figure 1

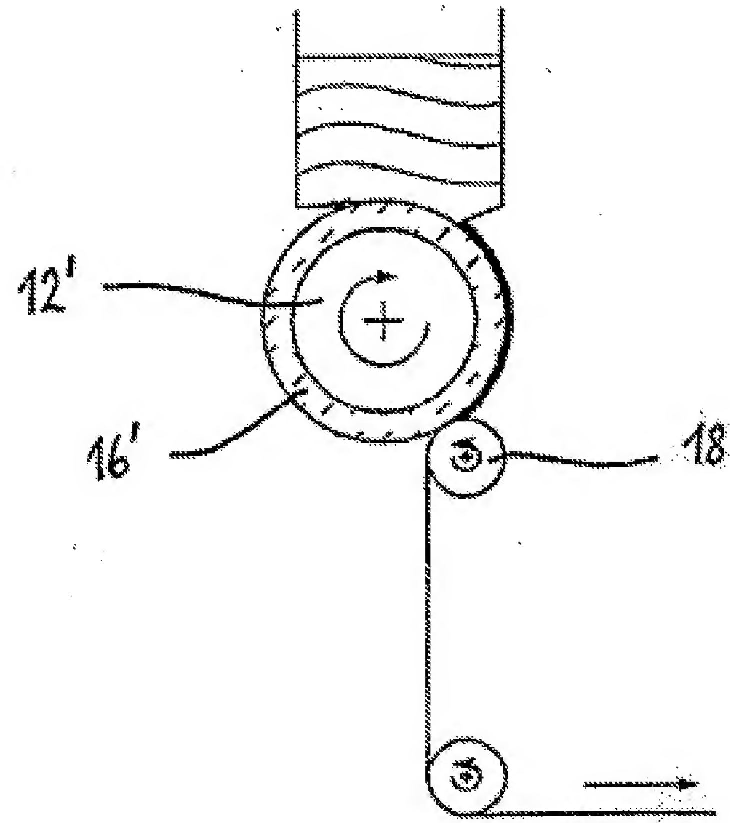

Figure 2

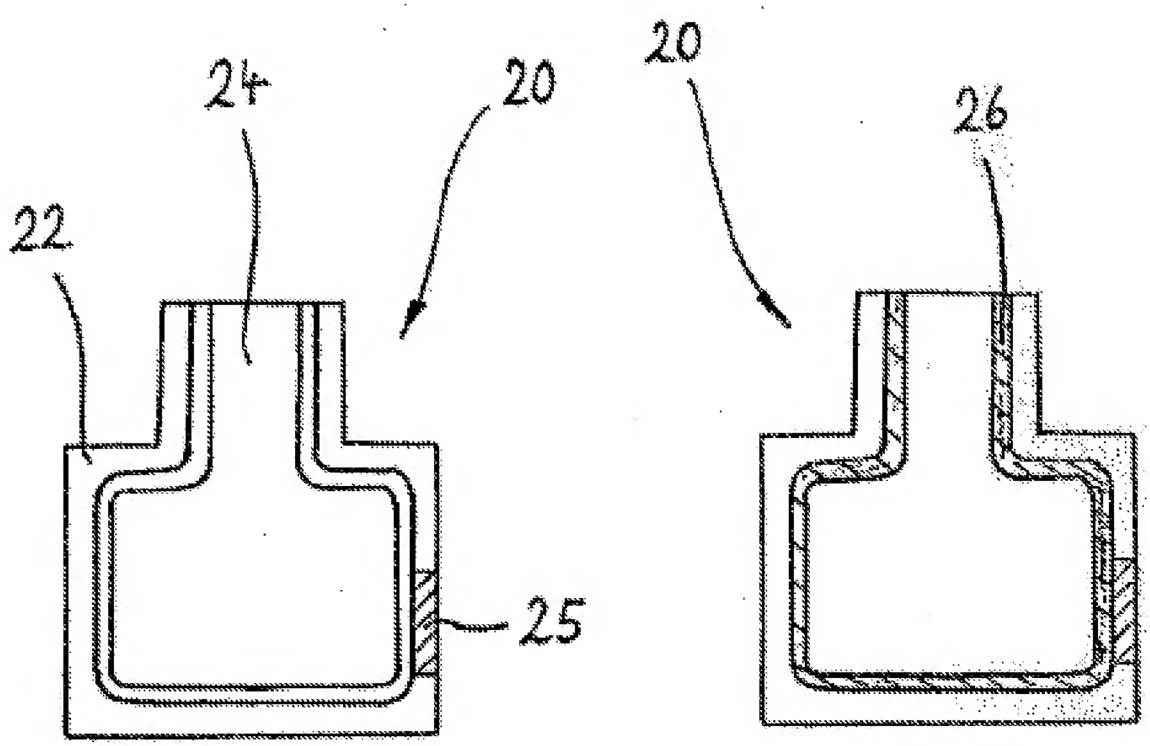

Figure 3

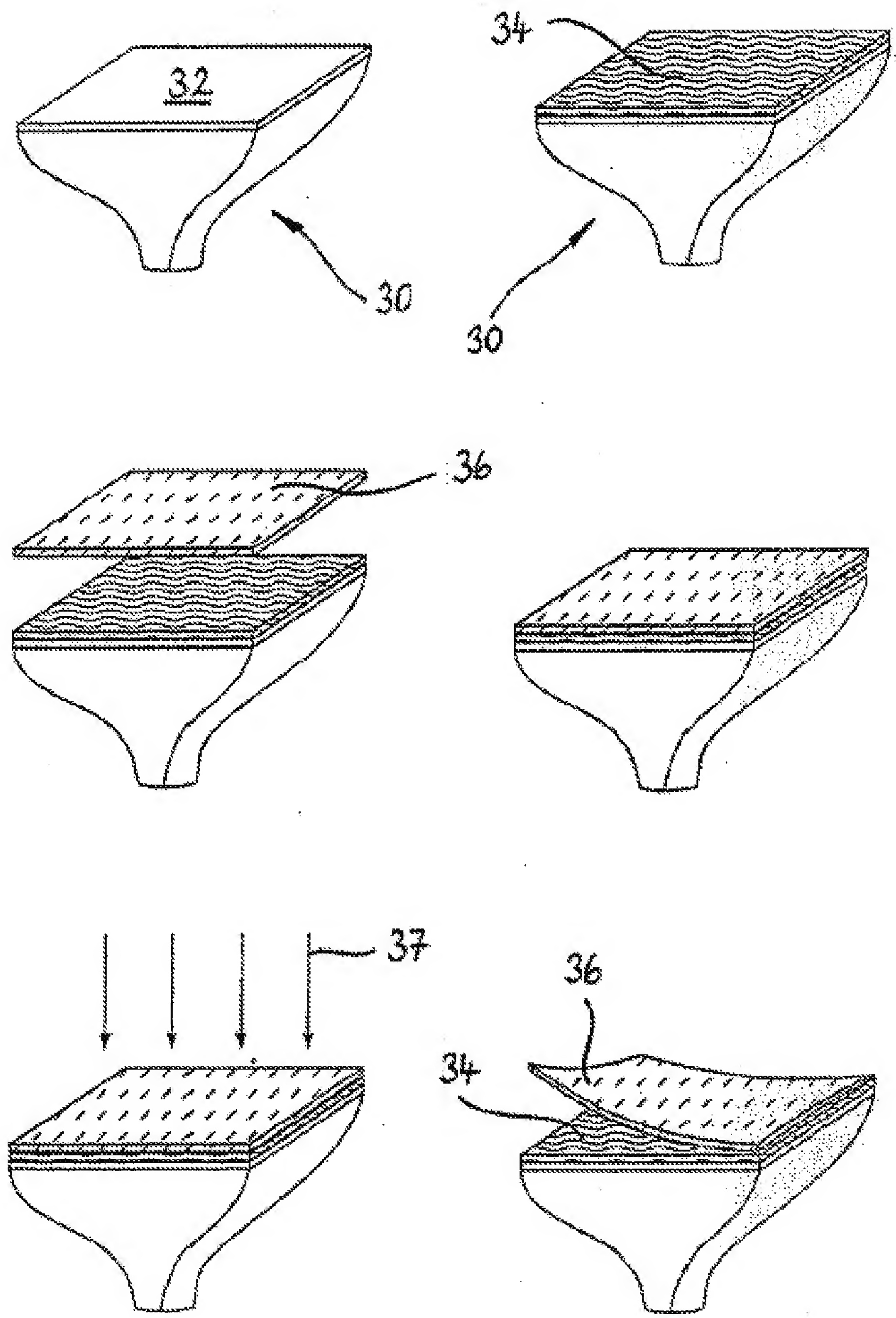

Figure 4